Developing A Model for the Determination of the Thermal Conductivity of High-Temperature Earth Minerals

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Introduction

Understanding the thermal properties of the minerals that make up the earth's mantle is important for understanding and modeling the earth at large. This is especially true when considering heat flow emanating from deep inside the earth, which is responsible for much of the dynamic behavior expressed at the earth's surface. The thermal conductivity of a material can be thought of as the efficiency of heat transport through the material due to a thermal gradient. The thermal conductivity of a material is given by the heat flux through the material divided by the temperature gradient across the material.

$$k = \frac{Q}{A \times t} \times \frac{L}{\Delta T}$$

Where k is thermal conductivity measured in units of power per unit length per unit temperature, Q is heat flow measured in power per unit area, A is the cross-sectional area of the material, t is time, L is the length of the material in the direction of heat flow, and ΔT is the temperature difference across the material. An experimental apparatus for measuring thermal conductivity is shown in **Diagram 1**.

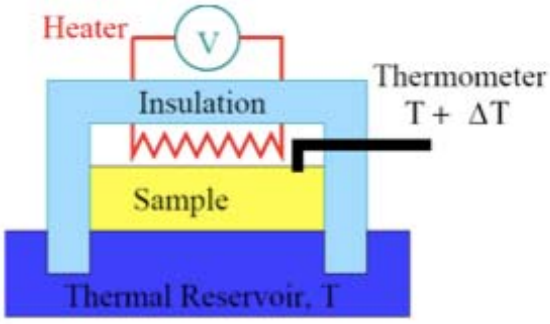

Diagram 1: Apparatus for measuring thermal conductivity (P. Allen, lecture notes, 2007, July 3.)

In such an apparatus one side of the material in question is held in thermal equilibrium with a thermal reservoir while the temperature of the other side is increased using a heater. The power output of the heater is measured as well as the temperature on both sides of a sample of known length and cross-sectional area and from this the thermal conductivity can be measured. Many experiments are carried out on high-temperature, high-pressure earth minerals in hopes of determining their physical characteristics, but

such an experiment using the above apparatus would be highly impractical, making experimental determination of the thermal conductivity of earth minerals at the high temperatures and pressures of the earth's mantle nearly, if not completely, impossible. Since we lack any means to experimentally measure thermal conductivity of minerals at the pressure and temperature conditions of the mantle, we must create a computational model in order to gain some insight into the problem.

Methods

In 1954-55 Fermi, Pasta, and Ulam performed a computational experiment on a dynamical, one-dimensional string of particles connected by springs that exerted non-linear forces on neighboring particles. If the particles had been connected by springs with simple, linear forces, the forces between particles would be given by Hooke's Law.

$$F = k(x_{i+1} + x_{i-1} - 2x_i)$$

Where F is the force between particles, k is a constant, and x_i is the displacement of the i^{th} particle from its equilibrium position. Considering a one-dimensional string of particles connected in such a way gives rise to simple harmonic motion of the string as shown in **Figure 1.** When the end-points of the model are fixed in place as in the Fermi, Pasta, Ulam problem, the model produces a string of particles that can vibrate as a standing wave. Note that displacements plotted along the vertical axis are actually horizontal displacements and are plotted on the vertical axis for clarity.

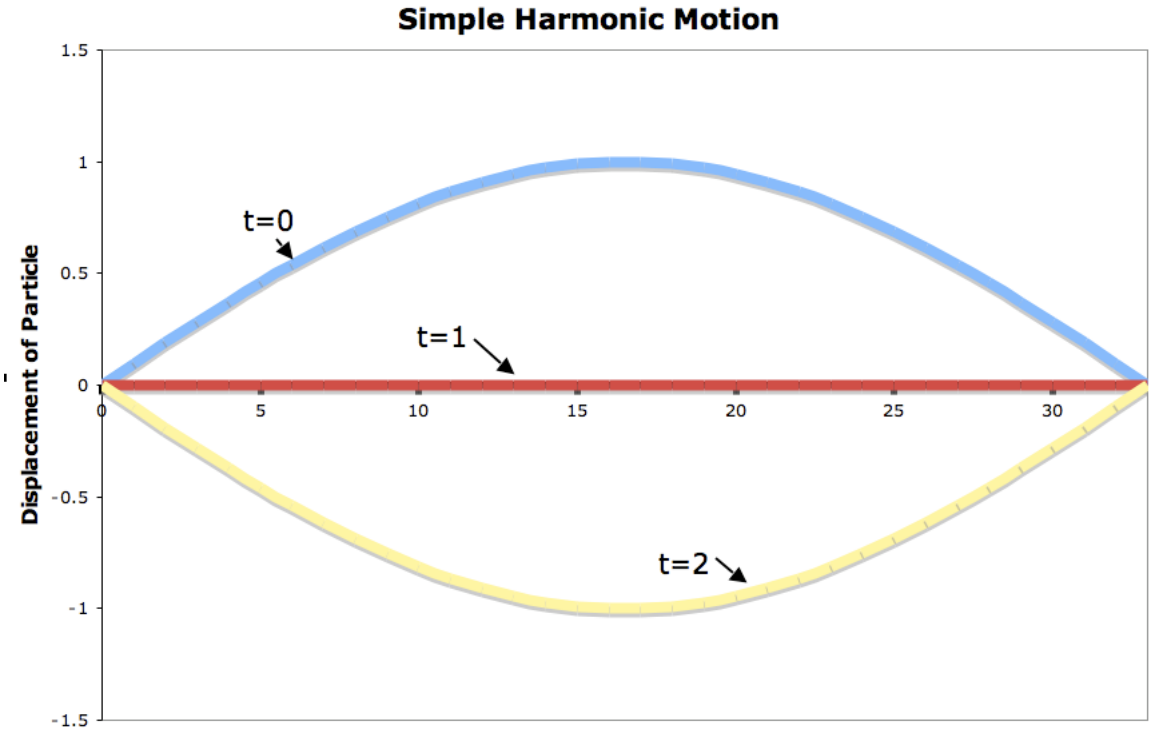

Figure 1: Simple Harmonic Motion in 1D Model.

However, Fermi, Pasta, and Ulam considered a string of particles that were connected by springs producing non-linear forces given by the following equation.

$$F = k[(x_{i+1} + x_{i-1} - 2x_i) + \alpha((x_{i+1} - x_i)^2 - (x_i - x_{i-1})^2)]$$

Where α was chosen to be 0.25, and initial conditions were chosen so that the non-linear contribution to the forces between particles was around one-tenth of the linear contribution. By adding this small, non-linear dependence on the displacement of the particles to the inter-particle forces, Fermi, Pasta and Ulam hoped to observe the partitioning of energy among the various degrees of freedom in their model. In a one-dimensional string of vibrating particles these degrees of freedom are all of the different normal modes of the vibrational movement. The normal modes of a system are the different configurations of the system at which each of the pieces of the system oscillate at the same resonant frequency. The first four normal modes for a one-dimensional string of particles are illustrated in **Figure 2.** In such a system, the frequency of the n^{th} normal mode, ω_n, is given by $\omega_n=2\sin(n\pi/2N)$ where N is the number of particles in the system.

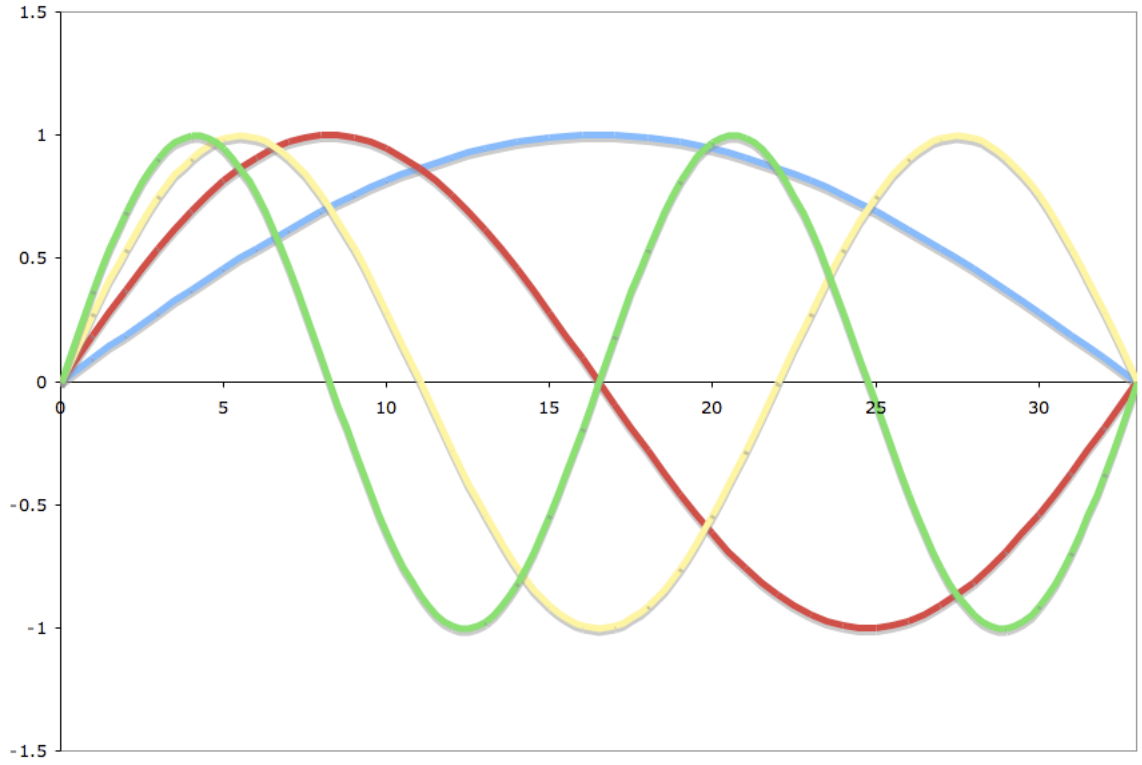

Figure 2: First Four Normal Modes of 1D Simple Harmonic Motion

Any configuration of the positions of the one-dimensional string of particles can be thought of as being a sum of the contributions to the particle positions from the different normal modes of the system. For simple harmonic motion, the amplitudes of the contribution of each normal mode to the total system, and by extension the contribution of each normal mode to the total energy of the system, is constant. However, as Fermi, Pasta, and Ulam saw in their experiment, adding the non-linear term into the equation for

inter-particle forces allowed the redistribution of energy among different normal modes. This happens when the amplitudes of the contribution from each normal mode to the system changes due to the anharmonicity introduced by making the force on the particles non-linear. The redistribution of energy among different normal modes as the experiment progressed is shown in **Figure 3**.

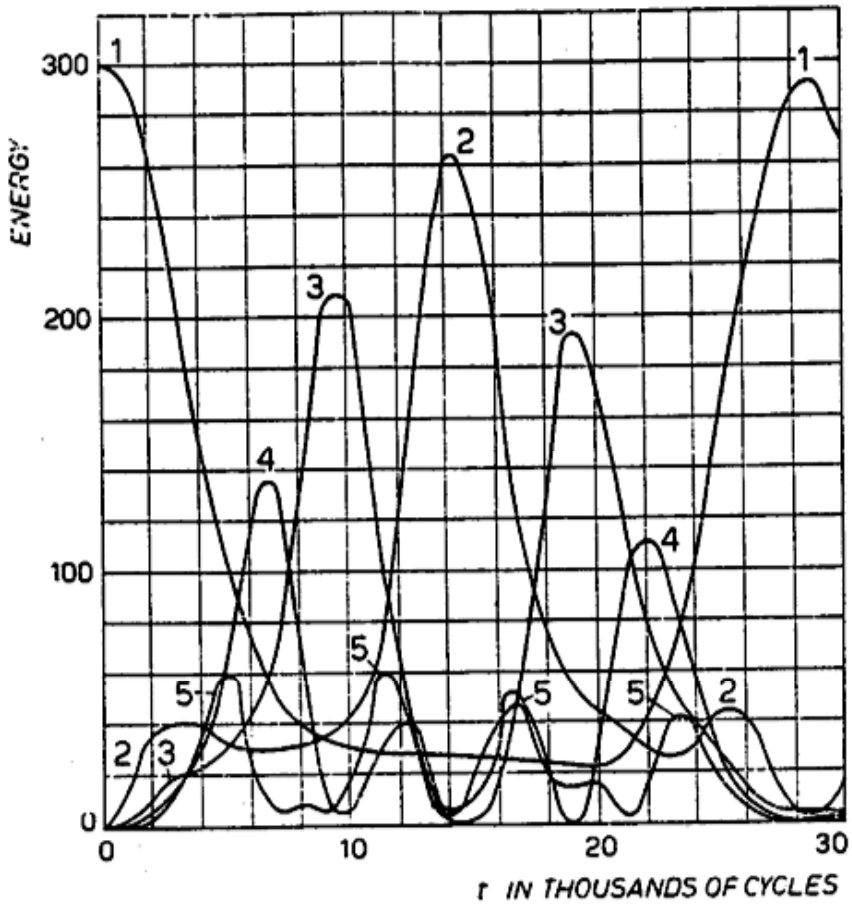

Figure 3: Distribution of Energy Among Normal Modes for FPU Experiment (Fermi, Pasta, and Ulam. 1955)

In **Figure 3** the contributions of the first five normal modes to the total energy is given for the system for 30,000 cycles of the experiment. In order to familiarize myself with the FPU problem, and in order to gain some basic experience in scientific modeling, I reproduced the results of the FPU problem and the results for the energy redistribution are shown in **Figure 4.**

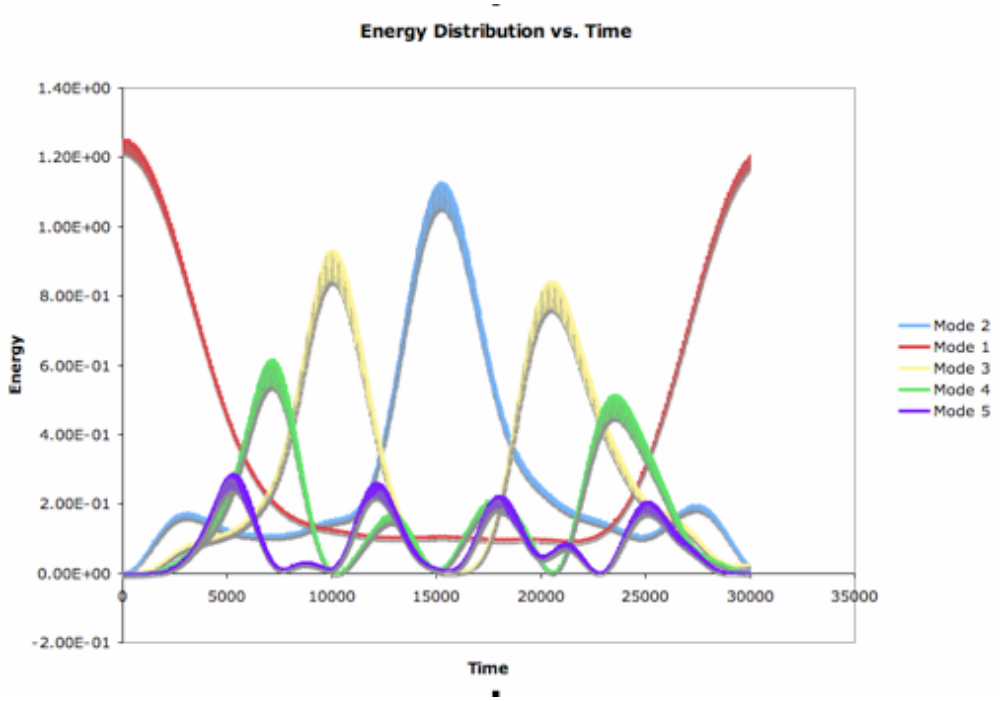

Figure 4: Reproduction of Results of Energy Distribution from FPU Problem

Compare these results with snapshots of the positions of the particles in the strings at various time steps as shown in **Figure 5**.

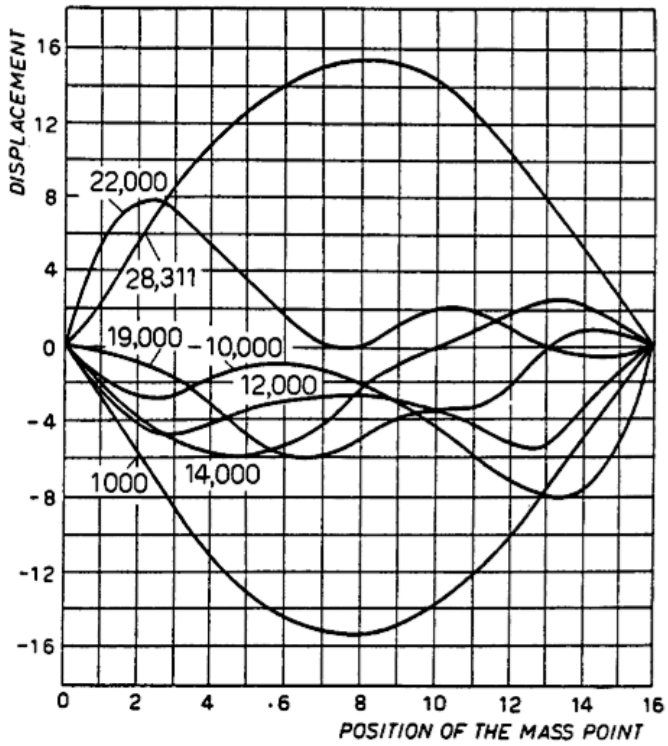

Figure 5: Positions of Particles in FPU Experiment (Fermi, Pasta, and Ulam. 1955)

On an atomic scale, real-world materials do not behave harmonically according to Hooke's Law. The jostling of particles in a real-world mineral could be broken down into the different normal modes of the crystal lattice; however, real-world materials behave anharmonically with energy being continually redistributed among different normal modes. The fact that energy is allowed to redistribute itself among the different normal modes suggests that the model considered by Fermi, Pasta, and Ulam may have potential as a model for investigating the thermal properties of high temperature minerals computationally.

In the following experiments the interparticle forces were determined using the Fermi, Pasta, Ulam model for a string of 130 particles separated at equilibrium by 42 dimensionless units (**see the appendix for further information**). Setting the mass and spring constant arbitrarily to 1 we arrive at the following equation for the acceleration of each particle at any given time.

$$a_i = (x_{i+1} + x_{i-1} - 2x_i) + \alpha[(x_{i+1} - x_i)^2 - (x_i - x_{i-1})^2]$$

Where x_i is the displacement of the i^{th} particle from its equilibrium position. The positions and velocities of the string were initialized in order to start the system at a given temperature. For a given configuration of the system the position and velocity of the i^{th} particle are given in terms of the sums of the contributions from each normal mode by the following equations.

$$x_i(0) = \frac{1}{\sqrt{N}} \sum_q A_q \cos(q^* i + \phi_q)$$

$$v_i(0) = -\frac{1}{\sqrt{N}} \sum_q \omega_q A_q \sin(q^* i + \phi_q)$$

Where N is the total number of particles, ω_q is the frequency of the q^{th} normal mode, A_q is the amplitude of the q^{th} normal mode and ϕ_q is the phase of the normal mode. A_q and ϕ_q are given by random numbers distributed according to the following probability functions.

$$P(A_q) = \sqrt{\frac{w_q^{\,2} m}{4\pi k_B T}}\, e^{-\frac{m \omega_q^{\,2} A_q^{\,2}}{4 k_B T}}$$

$$P(\phi_q) = \frac{1}{2\pi}, \text{ where } 0 \le \phi_q \le 2\pi$$

Where m is the mass of each particle, k_B is Boltzmann's constant, and T is the temperature of the system. The probability functions were analyzed using the Box-

Muller Method in order to produce a set of normal mode amplitudes for a given temperature. Given a set of normal mode amplitudes, we can assign each particle a certain position and velocity and therefore start the system at a given temperature. After the initial positions and velocities of the string were determined, a Verlet algorithm (see following equation) was employed in order to determine each subsequent position of the string.

$$x_i(t+\Delta t) = a_i(t)\Delta t^2 + 2x_i(t) - x_i(t-\Delta t)$$

The time step, Δt, was set to 1/8 dimensionless units. The string of particles was modeled with periodic boundary conditions, meaning that the string was looped so that each "end piece" of the model was attached to the other "end piece". In this way we create an identical environment for the motion of each particle that you don't get when the end pieces are fixed in place. In addition, this allows for traveling waves to propagate through the string in a way that is not possible for a fixed end-point string. Positions of the particles in the system are shown for a given run of the experiment in **Figure 6**.

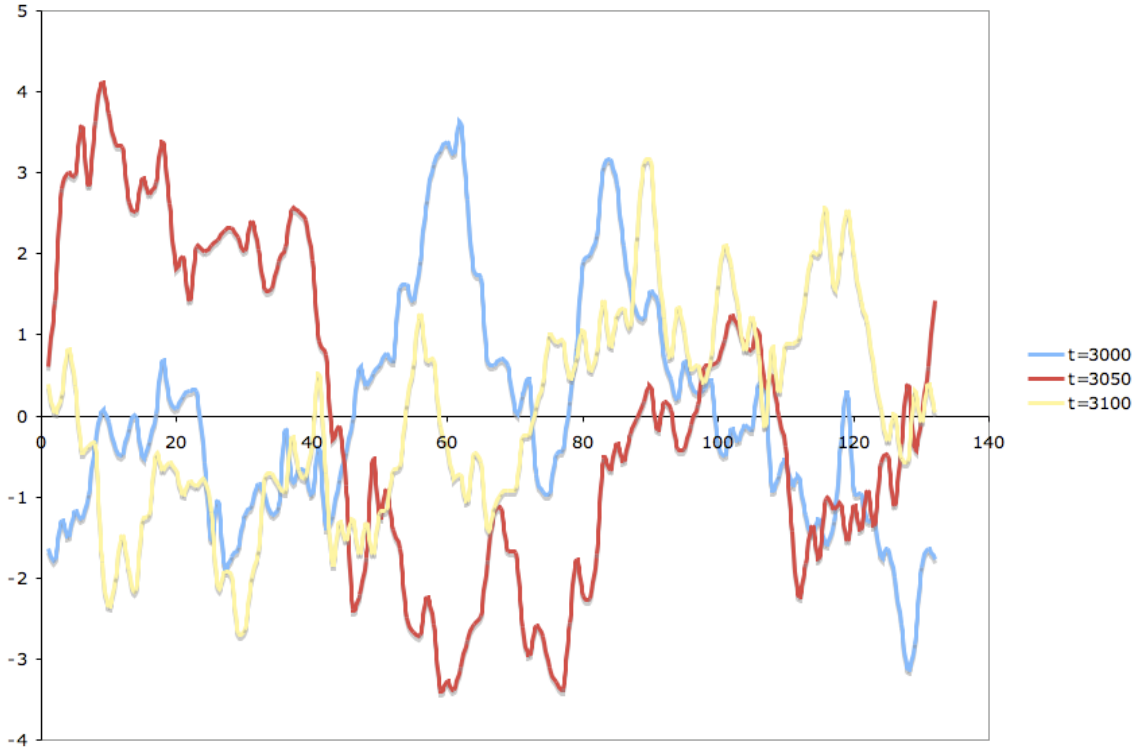

Figure 6: Positions of Particles With System Initialized to Given Temperaure

In **Figure 6** the experiment was initialized with $k_BT=0.125$ and with $a=0.25$. In all the runs of the experiment energy was calculated by summing the kinetic and potential energy of each particle of the string. Energy was conserved in the experiments usually within ~0.05%.

It is possible to look at how energy is moving through our string of particles by considering the energy current of the string. The energy current of the string can be determined by considering the energy contained within all of the particles of the system and the work that each particle is doing on its neighboring particles. The energy current is given by the following equation.

$$S = \frac{1}{L}\sum_i (\frac{1}{2} m v_i^2 + V_i) v_i - \frac{1}{L}\sum_i (u_i - u_{i+1}) \frac{\partial}{\partial x_i} V(x_{i+1} - x_i) v_i - \frac{1}{L}\sum_i (u_i - u_{i-1}) \frac{\partial}{\partial x_i} V(x_i - x_{i-1}) v_i$$

Where L is the total length of the string (i.e. the equilibrium distance between particles, 42, times the number of particles), V is the potential energy of each particle due to neighboring particles, and u_i is given by the following equation.

$$u_i = i\sigma + x_i$$

The first term represents the energy current due to the movement of each particle and the energy contained within each particle. The second term represents the work each particle is doing on its neighboring particles (i.e. the displacement derivative of the potential energy times the actual distance between particles.

There is another way to calculate energy current that we used to check the accuracy of our formulation of energy current. It is given by the following equation.

$$S = \sum_q (\frac{1}{2} m \omega_q^2 A_q^2 \frac{d\omega_q}{dq})$$

Where the quantity $\frac{1}{2} m \omega_q^2 A_q^2$ represents the energy due to the contribution of the q^{th} normal mode to the positions and velocities of the system and the quantity $\frac{d\omega_q}{dq}$ gives the velocity of the q^{th} normal mode. The amplitude of each normal mode is calculated at any given time by the following equations.

$$\tilde{A}_q = \sqrt{\frac{1}{N}} \sum_\ell (x_\ell + i \frac{v_\ell}{w_q}) e^{i q \ell a}$$

Where $i=(-1)^{1/2}$ and l now represents the position of a particle along the string. In order to convert the amplitude into a real number we simply consider the real and imaginary parts of $\tilde{A}_q$. If…

$$\tilde{A}_q = \alpha + \beta i$$

… then…

$$A_q = \sqrt{\alpha^2 + \beta^2}$$

Which can be used in the equation written above to determine the energy current of the system. The two calculations were found to agree very well over long time periods, but had small variations over shorter time periods. The two calculations for energy current for a given experimental run are shown below in **Figure 7** for a long time period and in **Figure 8** for a short time period.

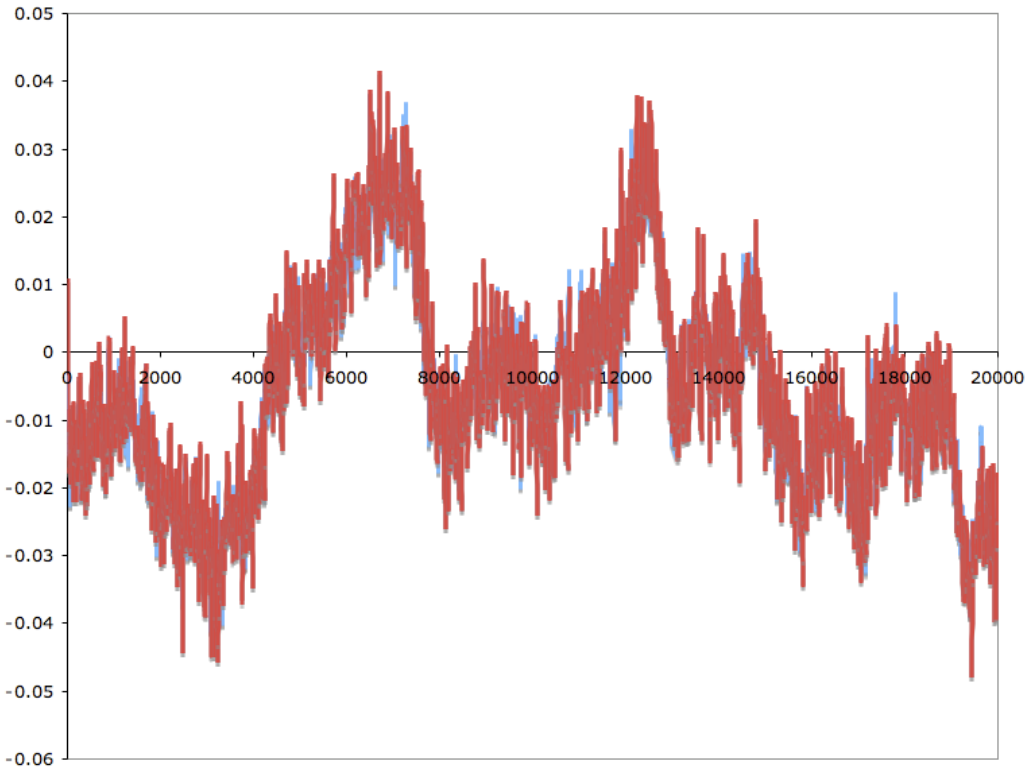

Figure 7: Energy Current from t=0 to t=20000

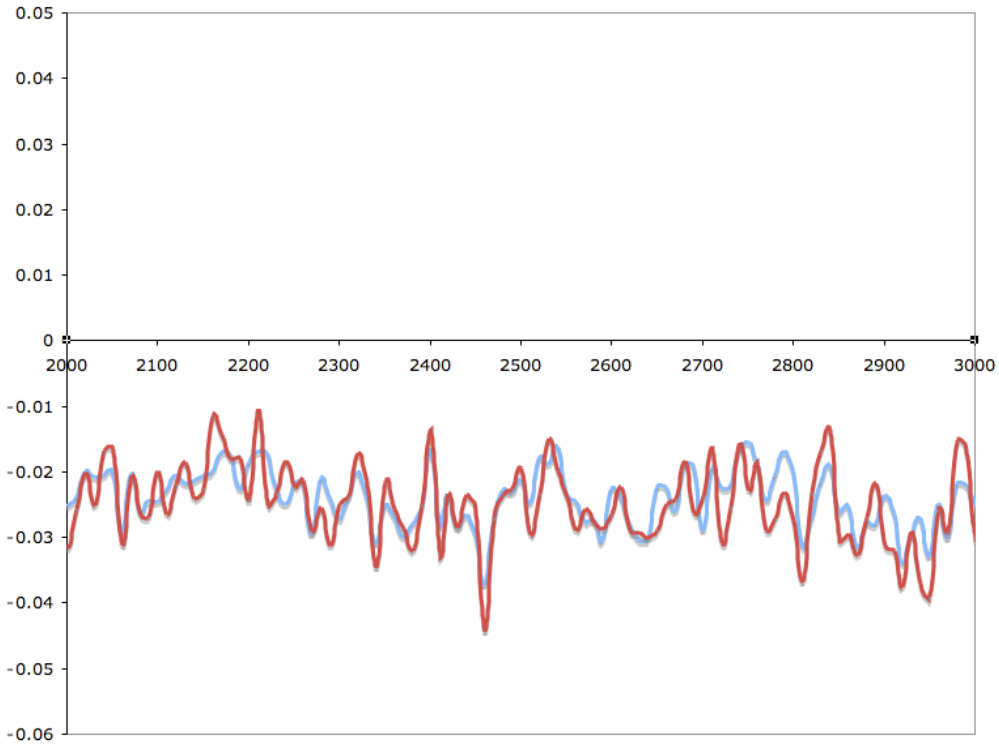

Figure 8: Energy Current from t=2000 to t=3000

In each of the graphs the energy current calculated from the normal mode amplitudes is shown in red and the energy current calculated from the Newtonian energy of the particles is shown in blue. Though the two calculations agree well over long time periods, there are inescapable differences between the two for short time periods that must be addressed. The energy current calculated from the normal mode amplitudes is technically valid only for harmonic situations and is only an approximation for our situation given the anharmonic nature of our model. The other calculation of energy current is exact given that it is based solely on the Newtonian definition of the energy that can be ascribed to each particle. Thus, for the next phase of our experiments we considered only the energy current calculated from the sum of the Newtonian energy of the particles. In addition, the energy current given by the normal mode amplitudes is much more time consuming to calculate, making further calculations on the energy current based on this method too cumbersome for the time being. One check we performed on our calculations of energy current and on the experiment in general was to decrease the time step used in our experiment in order to ensure the accuracy of the positions and velocities given by our Verlet Algorithm. We repeated our experiment with time steps of $\Delta t=1/8$ and $\Delta t=1/22.6$ and calculated the energy current for each experiment. The results are shown in **Figures 9** and **10**.

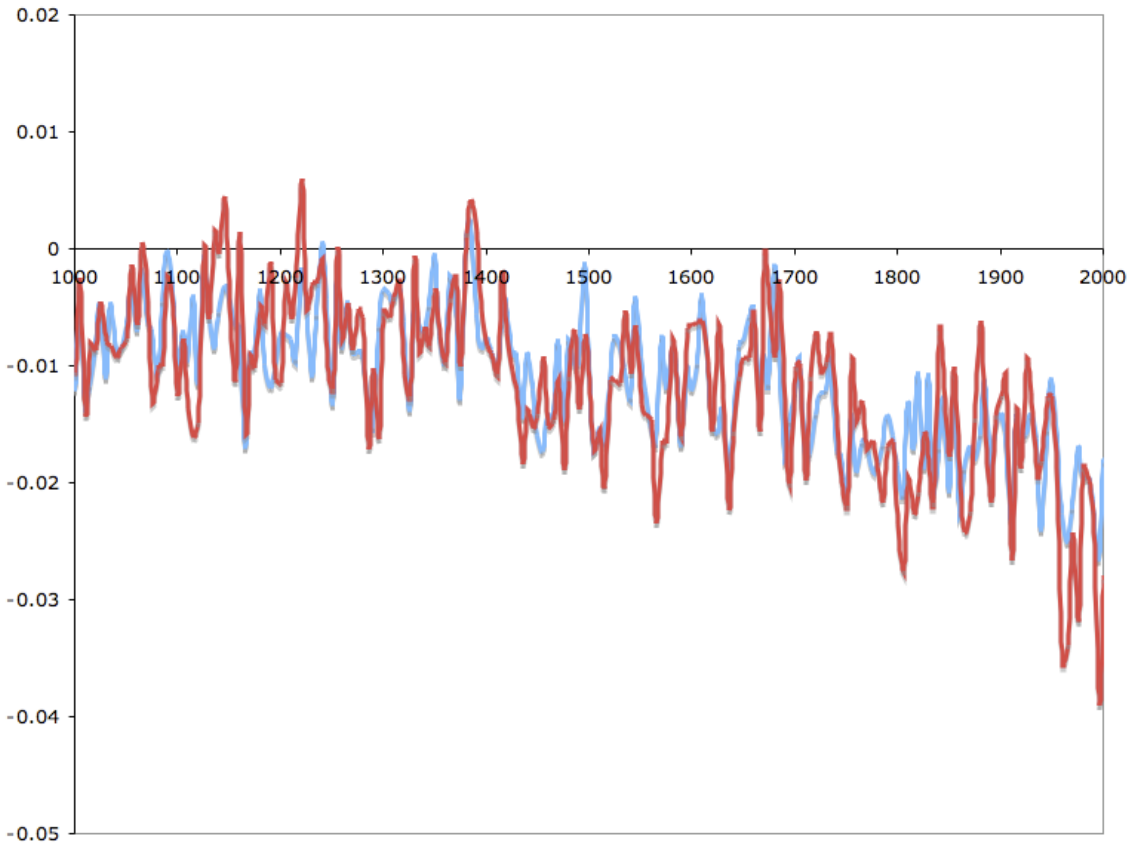

Figure 9: Energy Current Calculated with $\Delta t=1/8$

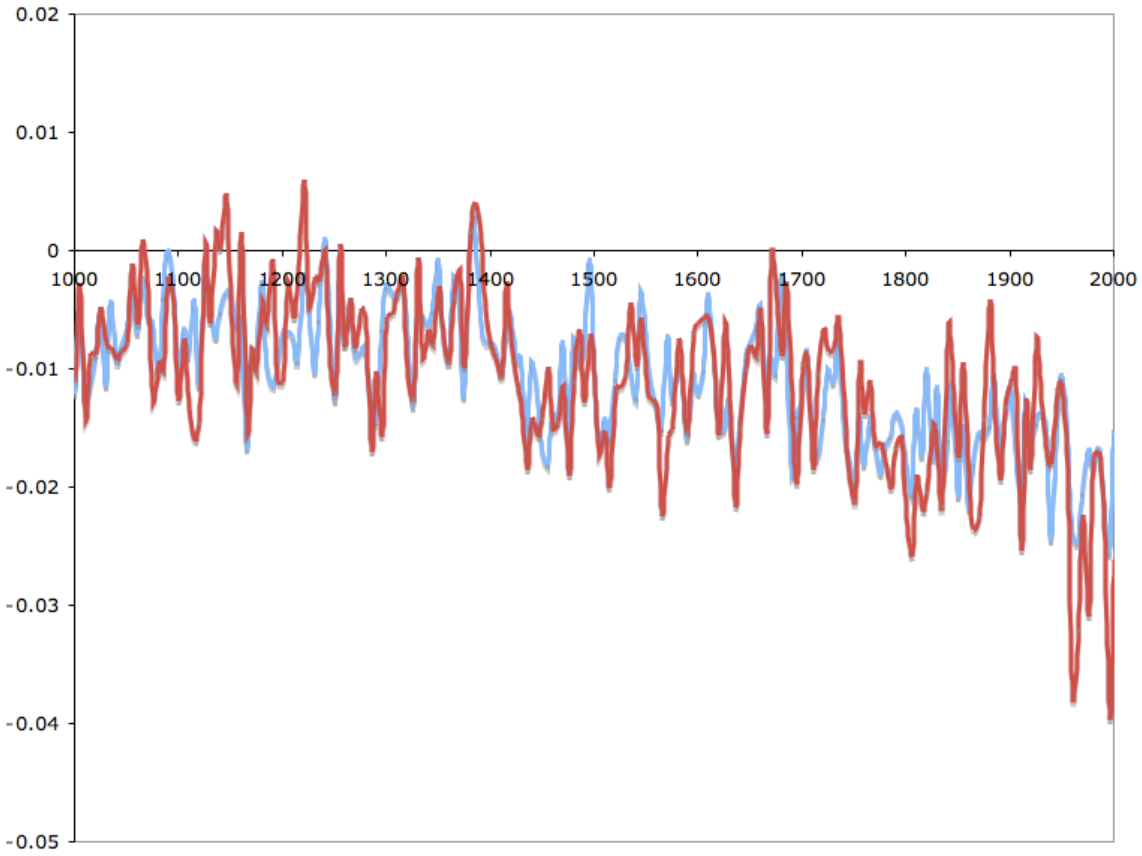

Figure 10: Energy Current Calculated with Δt=1/22.6

The two runs performed with different time step produced almost exactly the same results over the period shown, suggesting that there were no problems with our chosen time step for our experiments. We performed another check on the validity of our calculation of energy current by setting the coefficient of the non-linear term in our acceleration equation, a, equal to zero. By doing so we create a simple harmonic oscillating system which is expected to have a constant energy current. In fact this is what is observed which further confirms our calculation of energy current.

Eventually, we conducted ten runs of the experiment, each initialized with the same conditions as before. However, our method of initializing the experiment to a certain temperature involves a semi-random assignment of normal mode amplitudes, causing the actual energy, E, of each of the runs to vary slightly from the expected mean value of Nk_BT. In order to standardize the runs, the initial energy was calculated using the given normal mode amplitudes to initialize the string. The system was then reinitialized by multiplying each of the normal mode amplitudes by a factor of $(Nk_BT/E)^{1/2}$. This caused the energy of each run to agree with a maximum deviation from Nk_BT of about 1.5%.

The next calculation we made was for the energy current correlation function.

$$\langle S(t)S(t+\Delta t)\rangle$$

The energy current correlation function calculation shows how energy current at a given time is correlated with values of energy current at varying values of time delays, Δt. The energy current correlation function is calculated by taking the average of the product of S(t) and S(t+Δt) over an interval of time (that is, for differing values of t) and then repeating this calculation for different values of Δt over the same time interval. In effect, the energy current correlation function tells how much time the system spends with a given energy current configuration, and in this way it is an indicator of the effectiveness of heat transport through the system. Consider the case of the experiment run with simple harmonic motion where the energy current is constant. If the energy current is constant then energy can be transported through the system unimpeded as quickly as the velocity of the traveling waves transporting the energy allows. In such a case, the energy current correlation function will also be constant and will be equal to the square of the constant value of energy current. However, when the string of particles is modeled as an anharmonic system it can be seen from **Figure 7** that the energy current is anything but constant and under such a condition the energy current correlation will drop off rapidly as Δt gets progressively larger. A more rapid drop off of the energy current correlation can be interpreted as representing a system in which energy current changes more rapidly, which, in turn, can be interpreted as indicating that the system is less effective at transporting heat. The results of the calculations of energy current correlation for the ten runs of our experiment are shown in **Figure 11** and **Figure 12**.

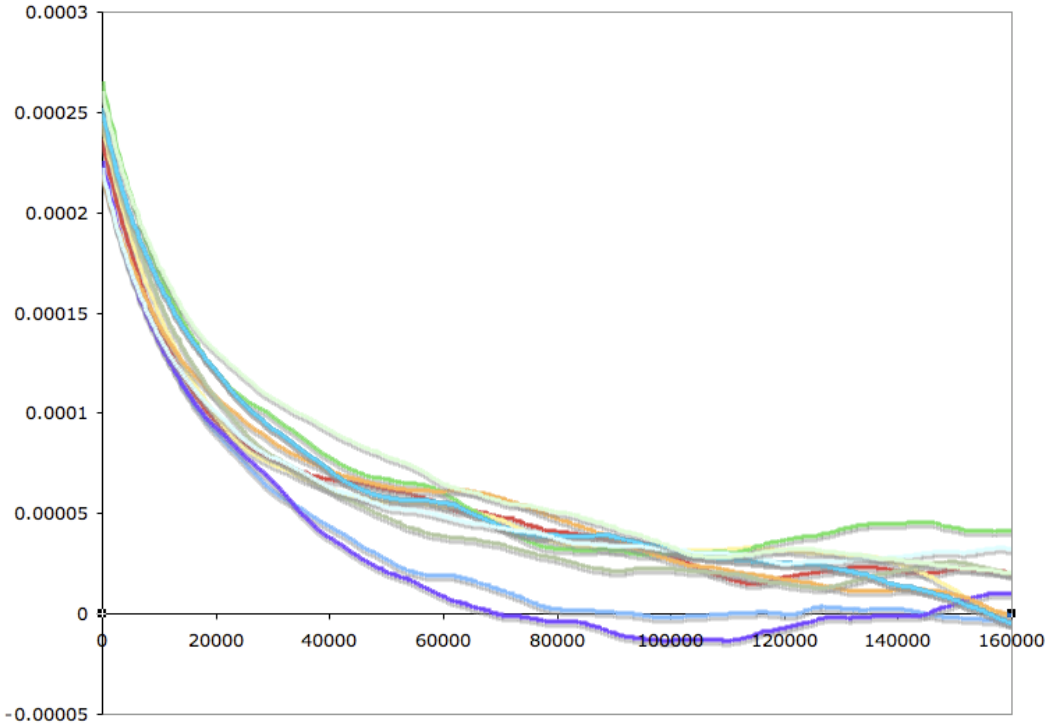

Figure 11: Energy Current Correlation from Ten Runs of Our Experiment

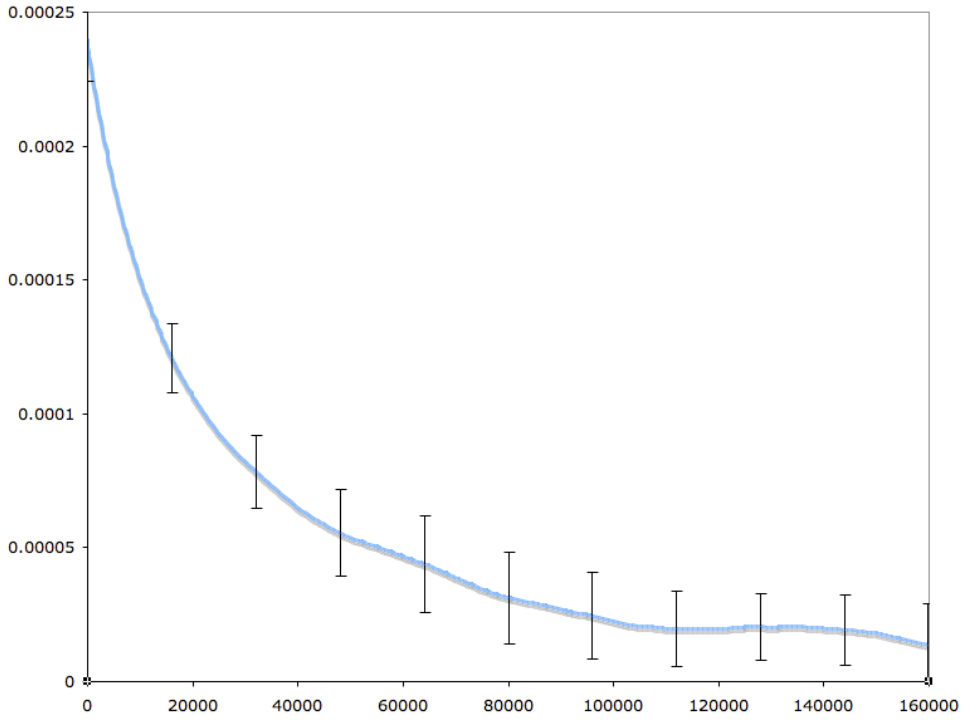

Figure 12: Average Energy Current Correlation for Our Experiment

As mentioned previously, the concept of the energy current correlation function is important for understanding the thermal conductivity of a system. In fact, the mathematical relationship relating the two values in a one-dimensional system follows.

$$k = \frac{1}{Lk_B T^2} \int_0^\infty \langle S(t)S(0) \rangle dt$$

Where L is the length of the system, k_B is Boltzmann's Constant, T is temperature, and k is the thermal conductivity of the system. If we could fit an exponential curve to our calculated energy current correlation function values then we could use the stated equation to determine a value for the thermal conductivity of our system. It was at this time that we decided to have a look again at the accuracy of the Verlet Algorithm we used in this experiment in order to determine if this had anything to do with the accuracy of the energy current and the energy current correlation functions that we had produce.d. Once again we decreased our value of Δt and calculated the energy current for a given run of our experiment. However, this time we also significantly increased the length of time over which we compared the different calculated values of energy current using the different values of Δt. What we saw was quite surprising and quite disheartening. When the calculations for differing Δt values were observed over longer lengths of time than previously the values calculated for energy current were found to diverge much earlier than we had hoped as shown in **Figure 13**.

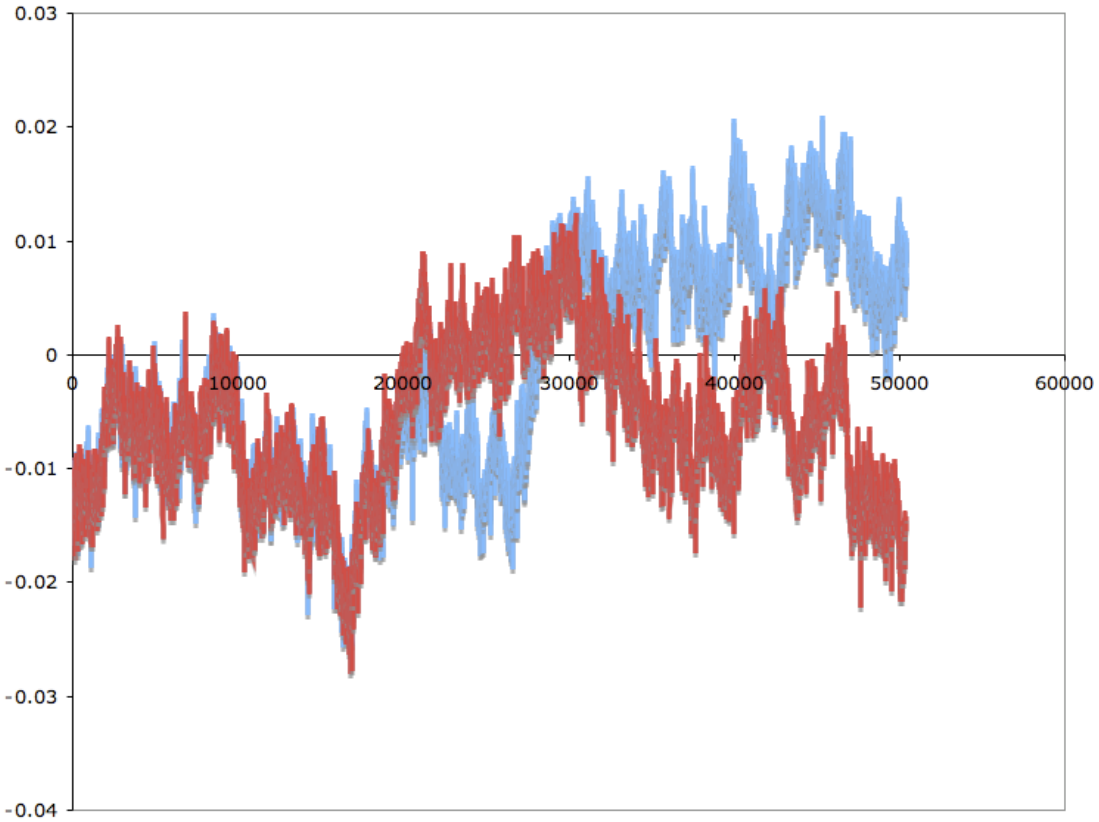

Figure 13: Energy Current Calculations for Δt=1/2048 (red) and Δt=1/4096 (blue)

It should be observed that the two calculations agree for a certain length of time before the errors in the Verlet Algorithm start compounding and then the values start drifting away from each other. The smaller the value of Δt the greater the length of time over which the Verlet Algorithm produces accurate results. Also, the smaller the value of Δt the longer the length of time a calculation of energy current agrees with a caculation of energy current made with an even smaller value of Δt . From **Figure 13** we can then assume that the calculation using $\Delta t=1/2048$ is accurate for about 20,000 units of real time and the calculation using $\Delta t=1/4096$ is accurate for an extra unknown length of time after which the Verlet Algorithm surely breaks down as well. This poses a serious problem because the energy current correlation functions from above were calculated up to 160,000 units of real time and the value of Δt was smaller than the calculations from **Figure 13** by a factor of 256 and 512. It is possible to decrease the value of Δt even further in order to increase the length of time over which our calculations are accurate. Then it would be possible to get accurate values for the energy current and the energy current correlation function which could ultimately be used to determine the thermal conductivity of our system. This, however, is a problem when you consider that each of the ten runs used to calculate our energy current correlation function took ~20 minutes to complete using $\Delta t=1/8$. In order to decrease the value of Δt and still be able to produce an accurate energy current correlation function it would also be necessary to increase the number of time intervals over which we invoke the Verlet Algorithm by the same factor that we use to decrease Δt which inevitably increases the length of time required to complete the calculation in real-world time. Increasing the accuracy of our calculations, therefore, is unfeasible at the present time. However, I will be passing this project on to Dr. Philip Allen's graduate student, Xiao Shen. My recommendations for further work on this project would be to determine an ideal value of Δt to insure accuracy of the Verlet Algorithm over the entirety of the experiment and recalculating energy current and the energy current correlation function using this new value. To do so, however, would require writing a program and sending it off for processing using some allotted time on a super-computer as the calculation is likely to be too time consuming for an ordinary desktop-like computer.

Bibliography

1. P. Allen. Lecture Notes, 2007, July 3.

2. E. Fermi, P. Pasta, S. Ulam, and M. Tsingou, *Studies of Nonlinear Problems I*, Los Alamos Scientific Lab. Technical report LA-1940, May 1, 1955.

Appendix on units and dimensions
(written by P. B. Allen)

The Fermi-Pasta-Ulam problem has three physical quantities with dimension, namely, the mass m and spring constant k of the harmonic problem, and the anharmonic spring strength k'. It is natural to let m define the unit of mass and $\omega^{-1}=\sqrt{(m/k)}$ define the unit of time. The harmonic problem has no natural unit of length; an oscillator's amplitude is a totally unconstrained variable in harmonic approximation. Anharmonicity introduces a natural unit of length, $k/k'=1/\alpha$. Fermi, Pasta, and Ulam chose the value of α to be 0.25. This is equivalent to choosing the unit of length to be $1/4\alpha$.

Heat current in a crystal introduces another unrelated unit of length, namely the distance between "atoms." This distance was totally irrelevant to the Fermi-Pasta-Ulam investigation of thermalization, because only displacements were examined, and the forces only depend on the Taylor expansion of the interatomic force law around equilibrium atom separation. But heat is transferred from one atom to another over an interatomic distance, and this greatly affects the heat current. We choose this distance to be 42 in units of $1/4\alpha$. The reason for this somewhat arbitrary choice is that it is the correct choice when the true interatomic potential is a Lennard-Jones potential,

$$v_{LJ}(r) = \varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - 2\left(\frac{\sigma}{r}\right)^{6}\right]. \qquad \text{(A.1)}$$

This potential has a minimum energy of $v=-\varepsilon$ at a distance of $r=\sigma$. The first derivative v' is 0 at $r=\sigma$. The next two derivatives are $k = v'' = 72\varepsilon/\sigma^2$, and $2\alpha k = v''' = -1512\varepsilon/\sigma^3$. Now we can use Fermi-Pasta-Ulam units $k=1/4\alpha=1$ to deduce that the interatomic distance, σ, should be set equal to 42. Of course, the notion of using Lennard-Jones rather than some other potential function is arbitrary, but it gives a sensible rationale for making a particular choice for σ.